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ABSTRACT

The conductivity of aqueous solutions containing 1 mM chloroform increases upon the chloroform decomposition that is induced by hydrodynamic cavitation in the suction-cavitation system. However, the rate of increase in conductivity (RIC) drops significantly, from 1.314 μS cm^{-1} min^{-1} without gas flow to 0.552 μS cm^{-1} min^{-1} with 25 mL min^{-1} of air flow. The RIC decreases further with increasing air flow, until pseudo-zero growth is reached at 200 mL min^{-1} air flow. Introducing O_3 at 33 mL min^{-1} gas flow (effective cavitation) improves RIC, from 0.4193 to 0.5509 μS cm^{-1} min^{-1}, but the enhanced rate (31.4%) is lower than at 200 mL min^{-1} of gas flow (little effective cavitation). The concentrations of dissolved O_2, O_3 and H_2O_2, that is formed on-site, increase with increasing gas flow and orifice plate hole diameter. Succinic acid (0.42 mM) is not oxidized by O_3 or H_2O_2 alone, but is rapidly degraded by a combination of O_3/H_2O_2 in the suction-cavitation system. The degradation rate of zero-order kinetics increases from 2.604 to 4.788 μM min^{-1} as orifice diameter increases from 5 to 8 mm. Increasing O_3 gas flow and temperature favour SA degradation. Increasing H_2O_2 concentration is more effective in producing OH radicals and promoting the oxidation of succinic acid than increasing O_3 input amount.

Keywords: Chloroform; Succinic acid; Decomposition; Ozonation; Hydrodynamic cavitation.

1. Introduction

Ozonation is an advanced oxidation process and, as such, is a common process for removing biologically toxic or persistent pollutants from waste water [1,2]. However, only low mineralization levels are achieved since by-products, such as small carboxylic acids, are generated during the process [3]. These by-products lead to COD and TOC reduction levels of less than 50% during the ozonation of dyes for 60-90 min, although decolourization is almost complete [4]. Ozonation is also moderately effective in removing COD from a sanitary landfill leachate [5]. Ozonation is therefore usually used as a pre-treatment to recalcitrance to improve biodegradation via partial oxidation [6,7]. A number of strategies, such as UV irradiation [8], ultrasound [9,10], microbubbles [11,12], specific catalysts [13,14] and H_2O_2 [15], have been combined to improve mineralization during ozonation and to achieve the highest COD and TOC removal efficiency [16,17]. The remarkable ozonation acceleration has been demonstrated in the presence of H_2O_2. TOC is simultaneously decreased because of the enhancement in hydroxyl radical ($OH^{\bullet}$) formation from the reaction of H_2O_2 with O_3 [18]. The reaction of O_3 with dissociated H_2O_2 is described as follows [19]:

$$H_2O_2 \leftrightarrow HO_2^- + H^+, \quad pK_a = 11.6 \qquad \textbf{(1)}$$

$$O_3 + HO_2^- \rightarrow OH^{\bullet} + O_2^{-\bullet} + O_2 \qquad \textbf{(2)}$$

A large number of organic contaminants have been efficiently removed using the O_3/H_2O_2 process [20-22]. Moreover, the O_3/H_2O_2 combination leads to important increases in the COD degradation rate in industrial wastewater treatment [23], indicating that $OH^{\bullet}$ formed on-site plays a critical role in the complete mineralization of organic contaminants. In view of $OH^{\bullet}$ formation, the hydrodynamic cavitation (HC) strategy has been regarded as another promising option with which to achieve ozonation process intensification.

HC is created during the turbulent flow of liquids and obtained when large pressure drops are generated within a moving liquid [24,25]. It is similar to the effects of ultrasonic cavitation; the thermal cleavage of H_2O and volatile chlorocarbons, as well as the formation of oxidative species, such as Cl_2, $OH^{\bullet}$ and H_2O_2, are induced by numerous hot spots [26,27]. Therefore, the degradation of organic contaminants by the high-energy micro-bubbles and nano-bubbles that are generated by HC have been extensively investigated [28-

32]. A HC reactor can be more easily scaled up to industrial scale than an ultrasonic reactor, although its higher energy efficiency has yet to be proven [24,33]. More interestingly, HC can significantly enhance other advanced oxidation processes (AOPs) [34,35], such as photocatalysis [36] and the Fenton process [37,38], allowing nearly complete degradation of organic substrates and a 76% reduction in TOC. Suction-cavitation (SC) is a HC process in which cavitation is generated at the suction side of the pump rather than at the pressure side. In our previous studies, SC exhibited improved energy efficiency over the classic HC on same scale [33].

The enhanced effects of HC on the ozonation degradation of organic contaminants and inactivation of microorganisms have been ever more frequently investigated in recent times [39-42]. The complete degradation of triazophos and 96% TOC removal has been achieved using a combination of HC and ozonation (HC/O_3) [42]. In most studies, HC can considerably promote removal efficiency, ozone utilization efficiency and reduce energy consumption and running costs, but little is known about the synergistic mechanisms of the HC/O_3 combination. Chloroform is one of the most frequently used model compounds because of its ultrasonic cavitation induced thermal decomposition. The thermal cleavage of chloroform can also be caused by HC processes, leading to a linear increase in conductivity with the decomposition of chloroform in aqueous solutions [27,33]. The influence of air and ozone/air flow on the HC-induced decomposition of chloroform has been observed in this study in order to reveal the existence of effective HC even under the interference of gas flow.

As mentioned above, the formation of refractory carboxylic acids results in lower organic contaminant mineralization with ozonation alone. Succinic acid (SA, HOOC-$(CH_2)_2$-COOH) is a dicarboxylic acid. It is a food additive, dietary supplement, excipient in pharmaceutical products and relatively stable to oxidants. It is also a common intermediate formed during the oxidative degradation of many organic compounds and cannot be removed by O_3 alone under acidic conditions [43,44]. Catalytic ozonation is therefore usually used to oxidise SA and achieve complete mineralization [13,17]. The $OH^{\bullet}$ oxidation rate constant of SA (3.1×10^8 M^{-1} s^{-1}) is much higher than its ozonation rate constants (less than 0.03 M^{-1} s^{-1}) at acidic pH [45,46]. SA has therefore been considered a good probe with which to identify oxidative degradation by $OH^{\bullet}$ rather than

78 molecular O_3 [13,45,47]. In this study, the degradation of SA is used to reveal the enhanced roles of HC on
79 the formation of $OH^{\bullet}$ in the presence of O_3 or O_3/H_2O_2 in the SC system.

80 **2. Experimental**

81 *2.1. Chemicals*

82 Succinic acid ($C_4H_6O_4$, Sigma-Aldrich, 99%), hydrogen peroxide (H_2O_2, Sigma-Aldrich, 50 wt. %),
83 phosphoric acid (H_3PO_4, Sigma, 85%), chloroform ($CHCl_3$, Riedel-de Haen, 99%), potassium
84 indigotrisulfonate ($C_{16}H_7K_3N_2O_{11}$, Sigma-Aldrich, analytical standard), potassium iodide (KI, Sigma-Aldrich,
85 99.5%), potassium titanium oxalate ($K_2TiO(C_2O_4)_2 \cdot 2H_2O$, Sigma-Aldrich, ≥90%) and deionised water (H_2O,
86 conductivity ≤1.5 μS cm^{-1}) were used as received.

87 *2.2. SC/O_3 setup*

88 This device consists of a Fischer ozon-generator 500 (Neckenheim, Germany) with a stabilized voltage
89 supply, and a device for creating HC by suction, as reported previously [40]. The SC device consists of a
90 centrifugal pump, a suction orifice, a heat exchanger, a water tank, a manometer, a flow-meter and some
91 connecting pipes. All of the materials that make contact with reagents are made from stainless steel (SS316).
92 The centrifugal pump (Speck GY-028-2, 2750 rpm, Roth, Germany) is capable of generating a pressure of
93 0.7 MPa and a maximum flow rate of 1980 L h^{-1}. The maximal electrical power was 1.1 kW. The total
94 solution volume was 800 mL. The bulk liquid temperature was maintained by a thermostat. Orifice plates
95 (thickness 1 mm, outer diameter 21 mm) with various single-hole diameters were attached at the suction side
96 of the pump so that the cavitation could be induced by suction. The inner diameter for the connecting pipes
97 was 21 mm. Cavitation events were controlled by orifice diameter. The suction pressure was measured by a
98 manometer and the flow rate through the various orifices was determined using a flow meter. The
99 hydrodynamic parameters of SC device are shown in Table 1.

100

101 **Table 1** Variation of hydrodynamic parameters with orifice plate aperture

102

The oxygen flow and pressure were set at 170 mL min^{-1} and 0.05 MPa, respectively, while the O_3/O_2 mixture was passed into the KI solution for 10 min. The O_3 yields were determined with various power settings. 50 or 100 mL min^{-1} of the O_3/O_2 mixture was typically introduced into the SC system and the rest gas was introduced into the 1 M NaOH solution for the removal of ozone and then was emitted the atmosphere.

2.3. Experimental procedures

Prior to the investigation of SA degradation, the influence of air and ozone/air flow on the decomposition of chloroform and the resulting increase in conductivity induced by SC were studied. The gas flow was sparged with a flow rate in the range of 0-300 mL min^{-1} into 800 mL of 1 mM chloroform in deionised water (pH 5.8) at the suction side of the pump at 20 °C. Meanwhile, the SC device, with a 5.0 mm-hole orifice plate, was started. The conductivity of the solutions was recorded for 20 min using an online conductivity meter (GMH3430) and the concentration of dissolved oxygen was recorded for 8 min using a dissolved oxygen meter (HACH LANGE HQ10).

The influence of gas flow on the concentrations of the dissolved O_3 and H_2O_2 that was formed in water was investigated using the following method; a gas flow containing O_3 was continuously introduced into 800 mL of deionised water in the SC system and the concentration of dissolved O_3 in water was periodically measured using the indigo method without interference from other oxidants [48]. The concentration of H_2O_2 that was formed on-site was detected using the $K_2TiO(C_2O_4)_2$ method without interference from other oxidants [49].

In a typical SA ozonation run, 800 mL of 0.42 mM SA in deionised water was circulated through the SC reactor for 90 min at 20 °C, while an O_3/O_2 gas flow was introduced into the solution under the suction orifice plate. The pH values were not artificially adjusted during ozonation. The initial pH value was 3.8. Aliquots (1 mL) of the processed solution were periodically extracted from the reaction system and the SA content was analysed using HPLC.

2.4. HPLC analysis

A Jasco LC-2000 Plus HPLC system was used to detect the concentration of SA. The HPLC system contains a DG-2080-53 3-Line Degasser, PU-2080Plus intelligent HPLC-pump, AS-2055Plus intelligent sampler, CO-2060Plus intelligent column thermostat, MD-2010Plus multiwavelength detector, LC-Net II/ADC and Chrompass Chromatography Data System, Vers. 1.8.6.1. A ReproSil-Pur C18-AQ (5 μm, 200 × 4.6 mm) column provided by Dr. Maisch GmbH (Ammerbuch-Entringen, Germany), 200 mM H_3PO_4 mobile phase and UV detection at 210 nm were used. Injection volume was 95 μL. Analyses were performed at a flow rate of 1.0 mL min^{-1} and a temperature of 20 °C.

3. Results and discussion

3.1. Influence of air flow on SC induced chloroform decomposition

Since it is quite difficult to cause the degradation of hydrophilic compounds such as carboxylic acids using cavitation processes [50], either the decomposition of chloroform and tetrachloromethane or the oxidation of potassium iodide were used to demonstrate the chemical effects of HC [26]. In our previous studies, the 5.0 mm-hole was demonstrated to be the optimal orifice plate aperture for chloroform decomposition in the SC system [33]. HC induced the thermal decomposition and mineralization of chloroform in aqueous solutions, resulting in the release of chloride and hypochlorite ions as well as a subsequent increase in conductivity. The conductivity of the aqueous solution linearly increased with chloroform mineralization, while any agitation weakened the cavitation events and chloroform degradation [51]. It is thus essential to investigate the influence of turbulence, which is induced by the introducing gas flow, on cavitation effects, i.e., chloroform decomposition driven by SC. Various air flows (0-300 mL min^{-1}) were sparged into 800 mL of 1 mM chloroform aqueous solutions at the suction side of the pump. The SC system was operated for 20 min to observe the variation in conductivity at 20 °C and the concentration of dissolved oxygen in the aqueous solutions was first recorded at 8 min. Fig. 1 shows the influence of air flow on conductivity and Fig. 2 presents the variation of dissolved oxygen in the aqueous solutions.

Fig. 1. Influence of introducing air flow on the conductivity of aqueous chloroform solutions in the SC system (800 mL of 1 mM chloroform, pH 5.8, 5.0 mm-hole orifice plate, 20 °C)

Fig. 2. Influence of introducing air flow on dissolved oxygen in aqueous chloroform solutions in the SC system (800 mL of 1 mM chloroform, pH 5.8, 5.0 mm-hole orifice plate, 20 °C)

As shown in Fig. 1, the conductivity of the aqueous chloroform solution increased with reaction time in the SC system without air flow, indicating that chloroform suffered decomposition under HC conditions and that chloride ions were released [27,33]. When lower air flow (25 mL min^{-1}) was introduced into the SC system, the rate of increase in conductivity (RIC) significantly dropped from 1.314 to 0.552 μS cm^{-1} min^{-1}. The RIC further declined with increasing air flow rate, until pseudo-zero growth was reached at 200 $mLmin^{-1}$ of air flow rate. There has been some discussion as to the impact of introducing a gas on hydrodynamic cavitation. On the one hand, the stabilized gas nuclei cannot play an essential part in hydrodynamic cavitation, which can readily occur via the generation of nuclei (*ab initio*) by certain forms of mechanical action [52]. On the other hand, gas-filled bubbles grow to visible size and then remain stable while vapour filled bubbles expand and collapse explosively [53]. It would appear that the rising temperature, namely air-nuclei in water, gives rise to cavitation, but attenuates the intensity of collapsing bubbles and reduces the cavitation effectiveness. Overall, the efficiency of SC is gradually attenuated with increasing air flow rate, but efficient SC still exists at lower gas flow rates in the SC system.

The amount of dissolved oxygen in the aqueous solutions decreased under suction and the higher air flow relieved the loss of dissolved oxygen (Fig. 2). This implies that increasing air flow and dissolved gases in aqueous solution work against increasing HC efficiency.

3.2. Effect of orifice plate on dissolved O_3 and H_2O_2 formation in water

Molecular ozone is known for its high selectivity to alkene bonds and unsaturated aromatic compounds. The decomposition of O_3 leads to more reactive and low selectivity species, $OH^{\bullet}$ as well as H_2O_2, in water [1]. Subsequently, the reaction of O_3 with dissociated H_2O_2 produces more $OH^{\bullet}$ [18,19]. Using HC to accelerate O_3 decomposition and form $OH^{\bullet}$ and H_2O_2 is therefore favourable to the oxidative degradation of

refractory pollutants in wastewater treatment. The effect of HC on the concentration of the dissolved O_3 and H_2O_2 formed in water was investigated in this study.

50 and 100 mL min^{-1} of gas flow containing 12 mg L^{-1} O_3 were introduced into 800 mL of deionised water for 20 min at 20 °C in the SC system, and the concentration of dissolved O_3 in water was periodically measured using the indigo method without interference from other oxidants [48]. The results are presented in Fig. 3A and 3B.

Fig. 3. Influence of orifice plate on the concentration of dissolved O_3 in water (800 mL of deionised water, 50 or 100 mL min^{-1} of gas flows containing 12 mg L^{-1} O_3, 20 °C).

(A: 50 mL min^{-1} of introducing gas flow)

(B: 100 mL min^{-1} of introducing gas flow)

As shown in Fig. 3A and 3B, the larger orifice plate aperture favours the dissolution of O_3 in water at the same amount of O_3 introduced. Similarly to the dissolution of O_2, the intensive SC effect induced by the 5 mm-hole does not lead to a higher concentration of dissolved O_3 in water. On the one hand, the cycle number is much higher with the larger aperture than with the small aperture, leading to more frequent gas-liquid contact. On the other hand, the higher vacuum degree with smaller apertures results in the degassing effect. Moreover, intensive HC probably accelerates O_3 decomposition, resulting in the formation of more $OH^{\bullet}$ radicals and H_2O_2 in water. It is therefore critical to understand the influence of HC on the formation of H_2O_2 during aeration with O_3.

50 and 100 mL min^{-1} of 12 mg L^{-1} O_3-containing gas flow were respectively introduced into 800 mL of deionised water for 120 min at 25 °C with a 5-mm orifice plate or without a restrictor in the SC system, and the H_2O_2 concentration in water was periodically measured using the $K_2TiO(C_2O_4)_2$ method [49] without interference from other oxidants. Results are shown in Fig. 4.

Fig. 4. Influence of suction-cavitation on the concentration of H_2O_2 formed in water (800 mL of deionised water, pH=5.8, gas flow containing 12 mg L^{-1} O_3, F1: 50 mL min^{-1}; F2: 100 mL min^{-1}, 25 °C).

In comparison with the results obtained without a restrictor, the intensive HC induced by the 5 mm-hole orifice plate did not result in more H_2O_2 regardless of gas flow, as shown in Fig.4. It appears that the yields of H_2O_2 and $OH^{\bullet}$ are closely related to the concentration of dissolved ozone in the deionised water (pH 5.8); the higher concentration of dissolved O_3 in water leads to higher H_2O_2 and $OH^{\bullet}$ formation. Effective HC cannot therefore induce additional O_3 decomposition and produce more H_2O_2 and $OH^{\bullet}$ in the SC system. This phenomenon was further demonstrated by the investigation into the ozonation degradation of SA in this study.

Moreover, the H_2O_2 yield dropped when the H_2O_2 concentration reached a certain value during the aeration of ozone, indicating that a reaction occurred between O_3 and H_2O_2.

3.3. Oxidative degradation of chloroform and SA using O_3, H_2O_2 alone and O_3/H_2O_2 in the SC system

As mentioned in a previous discussion, neither chloroform nor SA react with molecular O_3 under acidic conditions [1,43], whereas they can be oxidized by $OH^{\bullet}$ [54], although they are very recalcitrant compounds in comparison to benzene and phenol. The ozonation of chloroform or SA can therefore indirectly reveal the enhanced role that HC plays in the formation of $OH^{\bullet}$ and H_2O_2 in the SC system.

Prior to the investigation of SA ozonation, 800 mL of 1 mM chloroform in deionised water was circulated with a 5 mm-hole orifice plate for 20 min at 20 °C in the SC system. Meanwhile, either 33 or 200 $mLmin^{-1}$ of gas flow containing 5 mg L^{-1} O_3 was introduced into the solutions in order to study the effect of O_3 on the HC induced decomposition of chloroform. The result is shown in Fig. 5.

Fig. 5. Effect of introducing O_3 on the conductivity of aqueous chloroform solutions in the SC system (800 mL of 1 mM chloroform, gas flow containing 5 mg L^{-1} O_3, 5 mm-hole orifice plate, pH 5.8, 20 °C).

As shown in Fig. 5, the conductivity of the 1 mM chloroform solution clearly increased under 33 mL min^{-1} of air flow in the SC system, indicating that chloroform suffered thermal cracking under the effective collapsing cavitation. The RIC with 33 mL min^{-1} of O_3-containing gas flow reached 0.5509 μS cm^{-1} min^{-1}, which is 31.4% higher than the value without ozone. By contrast, conductivity increased very slowly under 200 mL $min^{-1}$of air flow rate, indicating that little chloroform suffered thermal cracking under the weak cavitation effect. Surprisingly, the RIC under 200 mL min^{-1} of O_3-containing gas flow increased to 0.1169 μS cm^{-1} min^{-1}, which is 3.4 times higher than the value without ozone. It appears that OH radicals were produced to oxidize chloroform during ozonation even in the absence of effective cavitation, while the formation of OH radicals was not enhanced by effective cavitation during ozonation in the SC system. A more detailed investigation was carried out using another refractory substrate, SA.

800 mL of 0.42 mM SA in deionised water was circulated via various orifice plates for 120 min at 20 °C in the SC system. Meanwhile, 100 mL min^{-1} of gas flow containing 19 mg L^{-1} O_3 was introduced into the aqueous solutions under the effects of various orifice plates with 5, 6, 7 or 8 mm aperture. After 120 min ozonation, the concentration of SA did not significantly decrease regardless of the orifice plate used, indicating that SA is very stable towards O_3 and O_2 molecules, while HC is not capable of promoting the formation of $OH^{\bullet}$ during ozonation. In addition, SA was not degraded under HC alone due to the lower yield of $OH^{\bullet}$ [40].

The oxidation potential (1.78 V) of H_2O_2 is lower than that of O_3. Likewise, SA was not considerably oxidized by H_2O_2 alone for 90 min at 20 °C within the SC system, as shown in Fig. 6. Fortunately, SA was rapidly decayed with the combination of O_3 and H_2O_2 in the same system. Obviously, the reaction between O_3 and H_2O_2 exceedingly produces active species, such as $OH^{\bullet}$, leading to the oxidative degradation of SA. The effect of the orifice plate on SA oxidation using O_3/H_2O_2 should thus be investigated so as to explore the enhanced effects of HC on the formation of $OH^{\bullet}$ in the presence of O_3/H_2O_2.

Fig. 6. Comparison of SA oxidation by introducing O_3, H_2O_2 alone or O_3/H_2O_2 into the SC system (800 mL of 0.42 mM SA, 0.40 mmol L^{-1} O_3 or/and 4 mM H_2O_2, 100 mL min^{-1} of gas flow rate, 6 mm-hole orifice plate, 20 °C).

3.4. Effect of HC on the oxidative degradation of SA in the presence of O_3/H_2O_2

The aperture of the orifice plate in the SC system remarkably influences cavitation events, the decomposition of chloroform and the ozonation of phenol [33,40]. The 5 mm-hole has proven itself to be the best orifice plate aperture in this SC system, since collapsing cavitation dominates the decomposition of volatile compounds and ozonation of phenol. However, the concentration of dissolved O_3 in the water increases with increasing aperture size, as shown in Fig. 3A and 3B.

Fig. 7 presents the effects of orifice plate aperture on the oxidative degradation of SA with reaction time in the presence of O_3/H_2O_2. As shown in Fig. 7, the oxidative degradation of SA follows pseudo zero-order kinetics. The degradation rates (or rate constant) of SA were calculated to be 2.604, 3.024, 3.444, 3.654 and 4.788 μM min^{-1} with gradually increasing orifice diameters (5.0, 5.5, 6.0, 7.0 and 8.0 mm). The correlation coefficients of the integrated pseudo zero-order rate law (see equation 3) were from 0.975 to 0.998.

$$\frac{C_t}{C_0} = -\frac{k}{C_0}t + 1 \qquad \textbf{(3)}$$

where k is the degradation rate constant of SA (μM min^{-1}), C_t represents the concentration of SA at a given time (t), and C_0 represents the initial concentration of SA.

Fig. 7. Effect of orifice plate aperture on oxidative degradation of SA by O_3/H_2O_2 in the SC system (800 mL of 0.42 mM SA, 0.40 mmol L^{-1} O_3 and 4 mM H_2O_2, 100 mL min^{-1} of gas flow rate, 20 °C).

The SA degradation rate increased with increasing aperture size, which is consistent with the effect of aperture on dissolved O_3 and O_2 in water. The larger orifice plate aperture induces higher liquid flow leading to improvements in circulation, violent turbulence and the dissolution of O_3 or O_2 in water. The degradation

of SA is therefore closely related to the concentration of dissolved O_3 in the aqueous solutions rather than effective HC. In other words, the increasing concentration of dissolved O_3 induced by turbulence and the large orifices favour the formation of $OH^{\bullet}$ during the reaction of O_3 and H_2O_2, while the effective HC induced by small orifices plays little role in either the formation of $OH^{\bullet}$ or the ozonation degradation of SA in the presence of O_3/H_2O_2

3.5. Effect of O_3/O_2 gas flow and temperature on the degradation of SA using O_3/H_2O_2

In general, gas flow and solution temperature can essentially affect cavitation events. As mentioned above, introducing a gas into the SC system weakens and even eliminates the chemical effects of cavitation, but the concentration of dissolved O_3 increases with increasing gas flow. The higher gas flow is therefore favourable to the oxidative degradation of SA by O_3/H_2O_2 in the SC system. The SA degradation rates increased from 1.81 to 3.95 μM min^{-1} with increasing gas flow (50 – 200 mL min^{-1}) in the presence of O_3/H_2O_2, (see entries 1-3 in Table 2). In fact, there is little effective cavitation at 200 mL min^{-1} gas flow in the SC system. This again demonstrates that the increasing concentration of dissolved O_3 rather than effective HC enhances the oxidative degradation of SA by O_3/H_2O_2.

Table 2 Effect of gas flow, temperature and O_3 and H_2O_2 concentrations on the degradation of SA by O_3/H_2O_2 in the SC system (800 mL of 0.42 mM SA solutions, 6 mm-hole orifice plate, 90 min of reaction time).

Solution temperature is another critical factor in the formation and collapse of cavitation bubbles. The optimal temperature for the degradation of chloroform and ozonation of phenol in the SC system is 20 °C [33,40]. When solution temperature is too low, the collapse temperature is also low (see equation (4)). Higher solution temperature leads to a higher vapour pressure, which negatively influences the formation of cavitation and lowers the collapsing temperature (T_{max}) of cavitation.

$$T_{max} = \frac{T_0 p_a (\gamma - 1)}{p_v} \quad (4)$$

where T_0 is the solution temperature, p_a is the acoustic pressure at the initiation of collapse, γ is the ratio of specific heats of the dissolved gas or vapour, indicating how much heat is released from the gas during the adiabatic compression. p_v is the vapour pressure of the solvent [55].

However, SA degradation rates increased from 3.44 to 9.86 μM min^{-1} with rising solution temperature (20 – 30 °C) in the presence of O_3/H_2O_2, as shown in entries 2, 4 and 5 of Table 2. This indicates that the oxidation of SA by O_3/H_2O_2 is a classical thermal reaction rather than cavitation-driven reaction in the SC system.

Overall, factors that are adverse to effective cavitation, such as increasing gas flow and temperature, promoted the oxidative degradation of SA with O_3/H_2O_2 in the SC system, indirectly indicating that effective cavitation plays little part in the formation of $OH^{\bullet}$ in the presence of O_3/H_2O_2.

3.6. Effect of O_3 and H_2O_2 concentration on SA degradation using O_3/H_2O_2

The electric power of the O_3 generator varied at constant gas flow (100 mL min^{-1}) and 4 mM H_2O_2. The degradation rate of SA increased from 2.69 to 5.00 μM min^{-1} with increasing O_3 input concentration (0.25 - 1.13 mmoL L^{-1}), as shown in entries 2, 6 and 7 of Table 2. It appears that the degradation rate of SA increased by 86% when the O_3 input amount increased 3.5 times.

The initial concentration of H_2O_2 was varied while the gas flow (100 mL min^{-1}) and O_3 input (0.40 mmol L^{-1}) were held constant. The SA degradation rate increased from 0.8 μM min^{-1} at 1 mM of H_2O_2 concentration to 3.44 μM min^{-1} at 4 mM of H_2O_2 concentration, as shown in entries 2, 8 and 9 of Table 2. This means that the degradation rate increased 3.3 times when H_2O_2 input amount increased 3.0 times. Increasing H_2O_2 concentration is obviously more effective in the formation of $OH^{\bullet}$ and the oxidative degradation of SA than increasing O_3 input with the O_3 and H_2O_2 combination.

4. Conclusions

We conclude that introducing a gas flow significantly affects the decomposition of chloroform and the ozonation of SA in the presence of H_2O_2 in the SC system. The larger gas flow decreases the decomposition of chloroform and HC efficiency, but promotes the dissolution of O_3 and O_2 as well as the oxidation of SA under the O_3 and H_2O_2 combination in aqueous solution. Although efficient HC still exists under less than

100 mL min^{-1} air flow in the SC system, it is not capable of increasing the concentration of dissolved O_3 in water and promote the formation of H_2O_2 during ozonation..

In summary, the higher gas flow, larger orifice plate aperture, rising temperature, higher O_3 and H_2O_2 input amounts favour the ozonation of SA in the presence of H_2O_2 in the SC system. As for the enhanced effects of HC on the degradation of phenol and inactivation of microorganisms observed in previous studies, we speculate that the direct action of molecular O_3 in the numerous micro- or nano-bubbles induced by HC must play a vital role.

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